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MICROFILTRATION MEMBRANES WITH THE SELECTIVE LAYER BASED ON ZIRCONIUM DIOXIDE

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The effect of zirconium dioxide – polymer (binder) composite on the quality of the microfiltration selective layer is studied. The conditions for deposition of the membrane layer and its drying and firing are established. The characteristics of the porous structure of the obtained membranes are considered.

The production of ceramic membranes for micro- and ultrafiltration, as well as equipment based on these membranes is currently expanding. Ceramic membranes have several advantages over polymer membranes, which makes it possible to use them in specific conditions. Ceramic membranes do not replace the polymer ones, but rather complement them. The advantages of ceramic membranes are most obvious in the food, pharmaceutical, microbiological, and other sectors of industry, as well as in water preparation [1–3].

A ceramic membrane consists of a relatively coarsely dispersed substrate and a more disperse selective layer. Depending on the size of the disperse particles of the medium under separation, the microfiltration layer deposited on a ceramic membrane can function as an independent membrane or serve as an intermediate layer (sublayer) for deposition of the ultrafiltration layer, and in this case, the size of heterogeneities in the substrate should not exceed the sublayer thickness. In this case, a high-quality smooth and homogeneous microfiltration layer is formed, whose thickness usually varies within the range of 10–50 μm [4].

Microfiltration (MF) membranes are usually made of the same materials as substrates; however, the size of the metal oxide particles should be smaller.

A microfiltration layer is produced either by extrusion of pastes with different sizes of oxide particles or by the “enveloping” procedure, which implies the deposition of a suspension containing disperse particles of the selective-layer material. The contact between the suspension and the substrate generates capillary forces, which cause the disperse medium to flow into the dry pores of the substrate, whereas the solid-phase particles remain and concentrate on the surface, forming a thin layer. After drying and firing, a selective microfiltration layer with the required size of the pores is formed,

which is firmly bonded to the membrane substrate. The processes of the deposition of the suspension and especially the drying and firing processes should be meticulously monitored to avoid cracks and flaking of the layer. If the size of the suspension (slip) particles is small enough to let them penetrate into large pores of the substrate, the permeability of the composite consisting of the selective layer and the substrate decreases through the blocking of the substrate pores. In this case, one or several interlayers are deposited, decreasing from one layer to another the size of the slip particles.

The present study employed the following initial materials: zirconium dioxide powder with an average particle radius of around 0.5 μm (determined from sedimentation data in a centrifuge field at a rotational speed of the rotor of 120 sec^{-1}); zirconium dioxide sol; distilled water; sodium salt of carbomethyl cellulose (Na-CMC) made in the USA; polyvinyl alcohol (PVA) of grade 4P240G (Japan), 3% acetate groups with the polymerization degree 2400; methyl cellulose (MC) produced by the Khimprom Company (Ussol'ye), TU-6-05-1857–78. The specified polymers were used in the form of aqueous solutions of varying concentrations.

The size of the sol particles was determined by the method of quasielastic light dissipation on an FK-22 photon-correlation spectrophotometer. The viscosity of the composite consisting of powder with polymer was measured using a Reotest-4 rotation viscometer indicating the flow curve. The pore radius was determined using the method of pressurizing compressed gas through a membrane impregnated with a wetting liquid (the bubble method). Mercury porosimetry was used for the same purposes (Porosimeter 200).

The substrates for the deposition of microfiltration layers were tubular elements with respective inner and outer diameters equal to 9×10^{-3} and 5×10^{-3} m made of aluminum oxide.

Microfiltration membranes were obtained by applying a composite based on zirconium dioxide powder directly on

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the substrate. It should be noted that the powder used was highly aggregated, which was corroborated by a significant modification of the distribution of particle and their average radius (toward a significant decrease) as the rotational speed of an SV-3 sedimentograph rotor increased (i.e., with increased acceleration of the centrifugal force field). The size distribution of particles was determined for the maximum rotational speed of this device (120 sec^{-1}). In this respect, one can state that the average radius of zirconium dioxide powder is no more than $0.5 - 0.6 \text{ }\mu\text{m}$; therefore, in preparing a composition for the selective layer, the suspension ought to be stabilized not only with respect to its sedimentation, but with respect to aggregation as well, i.e., the aggregates existing in the suspension ought to be destroyed. Otherwise, it will be impossible to obtain selective layers with reproducible properties, and the selective-layer pores will contain both pores created by clearances between individual particles and pores produced by particle aggregates, which will lead to an extremely wide pore-radius interval. At the same time, the initiation of cracks and flaking of the selective layer becomes possible.

Three water-soluble polymers (Na-CMC, PVA, and MC) were tested in developing a composition suitable for deposition on the substrate. In the perfect case, the introduction of a polymer can accomplish several goals: ensure the required thickness of the selective layer through controlled viscosity, increase the sedimentation stability of particles due to the increased viscosity of the composition, ensure the aggregation stability of the suspension (prevent coagulation of particles), and, finally, prevent the formation of cracks in drying and calcination, due to the plastifying effect.

The viscosity of aqueous solutions of Na-CMC, PVA, and MC polymers, as well as compositions of ZrO_2 with these polymers was first measured to determine the relationship between effective viscosity and shear stress P .

The correlation of the flow properties of the compositions based on the polymers considered indicates that the viscosity of composites being equal (for a non-destroyed structure, i.e., at $P = 6 \text{ Pa}$), the minimum consumption of the polymer is observed in using Na-CMC. The final selection of the polymer can be made taking into account not only sedimentation stability but aggregation stability of the composition as well.

To assess the aggregation stability of the compositions, three samples of approximately equal viscosity (around $250 \text{ mPa} \cdot \text{sec}$ with $P = 6 \text{ Pa}$) of the following compositions were prepared: 1.1% Na-CMC – 15% ZrO_2 , 6.0% PVA – 10% ZrO_2 , 3.3% MC – 15% ZrO_2 . The composition of the PVA-based composite was determined by the propensity of such a system for stratification. Next, these composites were analyzed using a microscope before and after ultrasonic treatment.

It was found that all initial composites, even after thorough stirring, contain particle aggregates up to $50 \text{ }\mu\text{m}$ in size. The aggregates in the presence of MC are less dense than in

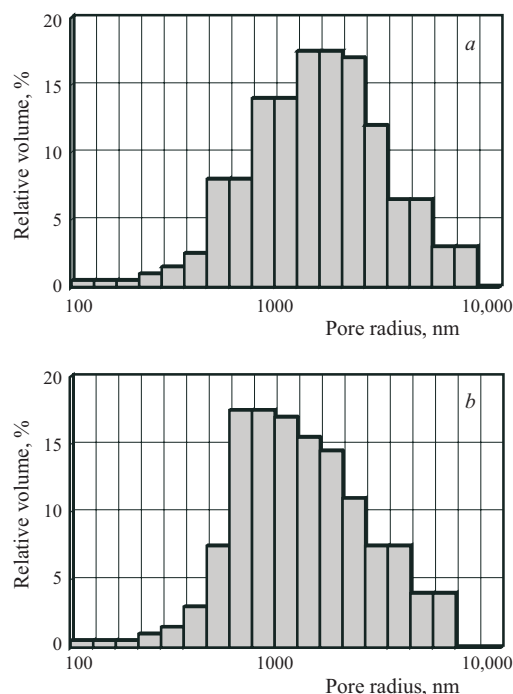


Fig. 1. Distribution of pores by radius in membranes 1 (a) and 2 (b).

the presence of PVA, and the composition based on Na-CMC contains both individual particles and loose aggregates. Ultrasonic treatment in all cases decreases the size of the particle aggregates, but in the presence of PVA the aggregates remain dense and individual particles are virtually absent. Ultrasonic treatment of mixtures based on Na-CMC leads to disintegration of aggregates into isolated particles, and the remaining aggregates become looser. The MC-based composition takes an intermediate position. Thus, the highest aggregation stability is observed in the compositions containing Na-CMC.

To determine the parameters of the selective layer, which can be obtained on the basis of the given zirconium dioxide powder, membranes without substrate were prepared using the first of the above-mentioned compositions (the composition additionally contained 1% glycerin of the total weight, and 1% SiO_2 of the zirconium dioxide weight; silicon dioxide was introduced in the form of sol as a sintering additive). Membrane 1 was prepared from a composite not subjected to ultrasonic treatment, and the composite for membrane 2 was treated for 2 min with ultrasound. The membrane calcination conditions were as follows: 1 h at 150°C , 1 h at 300°C , 1 h at 700°C , and 3 h at 900°C ; the rate of these temperature increases do not exceed 60 K/h . The results of the analysis of these membranes using the mercury porometry method are shown in Table 1 and Fig. 1.

It can be seen that ultrasonic treatment decreases the average pore radius by a factor of 1.5, and the pore distribution becomes somewhat narrower, which may be related to the decrease in the aggregate size compared to the initial suspen-

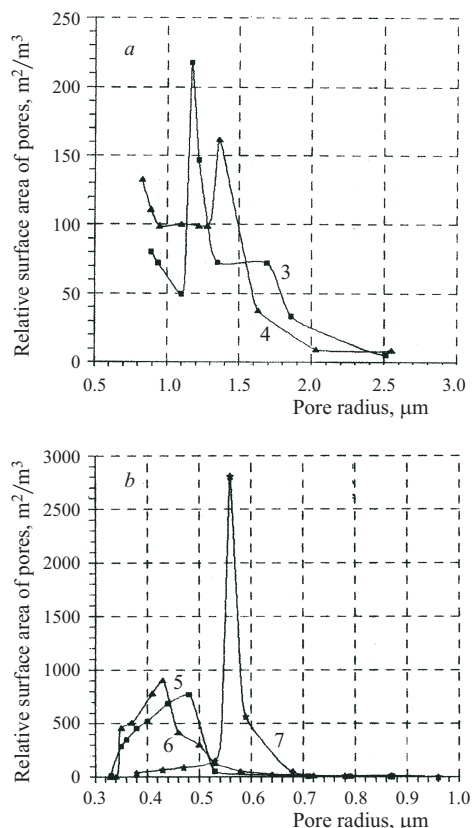


Fig. 2. Differential curves of radius distribution of pores in membranes 3 and 4 (a) and 5 – 7 (b). Curve numbers correspond to membrane numbers.

sion. On the other hand, the size distribution of pores is generally rather wide (the samples contain pores with a radius ranging from 0.2 to 8 μm), and the porosity reaches 60%, which is evidence of a distortion in the obtained data due to the existence of cracks in the selective layers. It should be noted that the emerging cracks make a contribution precisely in the specified radius interval (the coincidence here is purely accidental). It was impossible to avoid the initiation of cracks, since in order to produce a sample sufficient for mercury porosimetry, it has to be formed of a thick layer of the composite (several millimeters).

During the preliminary experiment, the composite of the same composition treated by ultrasound in an ultrasonic bath was deposited on a support to make an MF membrane (the calcination conditions were identical). Membrane 3 was obtained by applying the composite directly on the support, and

the support for membrane 4 was previously treated with a 0.5% solution of Na-CMC. The measurements of sample pore radii using the bubble method are shown in Fig. 2a. It can be seen that in spite of the high viscosity and concentration of the composites, a one-time deposition does not ensure the formation of an MF layer over the entire surface of the support. However, the differential curve segments within the pore radius range of 1 μm or less indicate that a selective layer has been formed on part of the surface (the share of pores with radius below 1 μm has increased). Judging from the shape of the curves, these membranes have two prevailing pore radii: the first one approximately correlates with the average radius of not entirely overlapped substrate pores, and the second one correlates with the MF layer with the average radius below 0.8 μm. At the same time, the share of small pores is higher in membrane 4 based on the substrate treated with Na-CMC than in membrane 3. It should also be noted that the large pores typical of the substrate persist as well (the maximum pore radius in membranes 3 and 4 is, respectively, 3.1 and 2.9 μm).

The microscopic study of the selective layer in membranes 3 and 4 revealed that a nonuniform layer of variable thickness (from 15 to 40 μm, occasionally less than 3 μm) with cavities up to 30 μm had been formed, but no big cracks were observed. Loose aggregates were visible in the layer.

One of the reasons for the established results (heterogeneity of the layer and its impregnability) can be the significant hydrophilicity of disperse zirconium dioxide, which prevents coagulation and gel formation in the composite layer adjacent to the substrate. The published sources usually note that the selective layer is formed out of gel arising on the surface of the substrate when part of the water is removed from the contacting composite via pores (the capillary effect) and due to the hydrophilicity of the substrate material. In our case, the hydrophilicity of zirconium dioxide is clearly higher than that of the support material (it was demonstrated earlier [5, 6] that zirconium dioxide gels are capable of self-dispersion), and gel formation does not occur (or more precisely, heterocoagulation does not occur). Hence it can be assumed that pretreatment of the substrate surface, the high viscosity of the composite, and, probably, multiple deposition of the composite are needed to obtain a non-absorbent layer.

Apart from the above-listed factors, one should note the existence of silicon dioxide sol particles in the considered composite, which under the specified conditions have a rather high negative charge, and their effect on the aggregation of zirconium dioxide particles has not been elucidated.

To verify the effect of particle aggregation (and the type of polymer) in the initial compositions on the parameters of membranes made on their basis, the three specified composites were deposited on substrates (before deposition the composites were treated by ultrasound for 2 min on a UZDN-A ultrasonic disperser at a frequency of 22 kHz; the composite was deposited by pumping as in all other cases). It was found that the MC-based composite is not absorbed in

TABLE 1

Membrane	Average pore radius, μm	Porosity, %	Specific volume of pores, cm³/g	Specific surface area of pores, m²/g
1	1.2	61	0.265	0.54
2	0.8	60	0.254	0.57

TABLE 2

Membrane	Composition	Pore radius, μm		Selective-layer thickness, μm
		maximum	average	
5	1	0.8	0.40	100
6	2	0.9	0.43	85
7	3	1.0	0.56	60

the substrate, and the other two composites are absorbed. In this respect, the MC-based composite was applied directly on the substrate, and the other two were applied after preliminary treatment of the substrate with a 0.5% Na-CMC solution. After drying and calcination (the same calcination conditions as in membranes without substrate), membranes were obtained whose the pore size was determined using the bubble method (Fig. 2b and Table 2).

The air permeability of dry membranes for a pressure difference of 0.1 MPa was as follows: $292 \text{ m}^3/(\text{m}^2 \cdot \text{h})$ for membrane 5, $302 \text{ m}^3/(\text{m}^2 \cdot \text{h})$ for membrane 6, $414 \text{ m}^3/(\text{m}^2 \cdot \text{h})$ for membrane 7, and $345 \text{ m}^3/(\text{m}^2 \cdot \text{h})$ for the substrate.

It follows from the specified data that the MF membranes in all cases have a certain excessive thickness, although their permeability is good. The latter fact points to the high porosity of the membranes, which is presumably determined by the presence of both individual particles and loose aggregates in the initial composition. This is also supported by the fact that for the given dispersion of the powder, the average pore radius in the absence of particle aggregates should have been smaller. Note also the rather narrow distribution of pores by radius (especially in membrane 7).

A further improvement of membranes can be accomplished by increasing the aggregate stability of composites by introducing stabilizing additives, which will bring about a

decrease in the pore radius together with a certain decrease in porosity. A decrease in the thickness of the selective layer can be accomplished by at least three methods: a decreased duration of contact of the composite with the substrate, a decrease in the solid-phase content in the initial composite, and forming a selective layer by multiple application of the composite with a variable composition. The second method appears to be the simplest. In this case, all parameters should be selected individually for each particular type of substrate, taking into account the nature of the material and its porous structure.

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